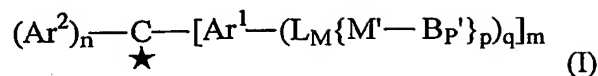


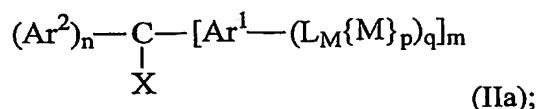
CLAIMS

1. A method of forming an ion of formula (I):

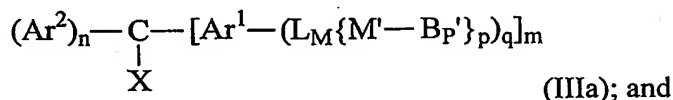


comprising the steps of:

- 5 (i) reacting a compound of the formula (IIa):



with a biopolymer, B_P , having at least one group capable of reacting with M to form a covalent linkage, to provide a biopolymer derivative of the formula (IIIa):



- 10 (ii) cleaving the C—X bond between X and the α -carbon atom of the derivative of formula (IIIa) to form the ion of formula (I);

where:

$\text{C}\star$ is a carbon atom bearing a single positive charge or a single negative charge;

X is a group capable of being cleaved from the α -carbon atom to form an ion of formula (I);

- 15 M is independently a group capable of reacting with B_P to form the covalent linkage;

B_P' is independently the biopolymer residue of B_P produced on formation of the covalent linkage;

M' is independently the residue of M produced on formation of the covalent linkage;

Ar^1 is independently an aromatic group or an aromatic group substituted with one or more A;

- 20 Ar^2 is independently an aromatic group or an aromatic group substituted with one or more A;

optionally wherein (a) two or three of the groups Ar^1 and Ar^2 are linked together by one or more L^5 , where L^5 is independently a single bond or a linker atom or group; and/or (b) two or three of the groups Ar^1 and Ar^2 together form an aromatic group or an aromatic group substituted with one or more A;

- 25 A is independently a substituent;

L_M is independently a single bond or a linker atom or group;

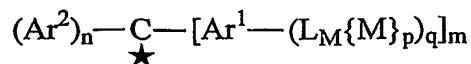
$n = 0, 1$ or 2 and $m = 1, 2$, or 3 , provided the sum of $n+m = 3$;

p independently = 1 or more; and

q independently = 1 or more.

2. A method of forming an ion of formula (I), comprising the steps of:

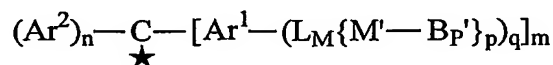
(i) reacting a compound of the formula (IIb):



X★

(IIb);

with a biopolymer, B_P, having at least one group capable of reacting with M to form a covalent linkage, to provide a biopolymer derivative of the formula (IIIb):



X★

(IIIb); and

dissociating X★ from the derivative of formula (IIIb), to form the ion of formula (I);

10 where:

X★ is a counter-ion to C★;

and C★, M, B_P', M', Ar¹, Ar², L_M, n, m, p and q are as defined in claim 1.

3. A biopolymer derivative of the formula (IIIa).

15

4. A biopolymer derivative of the formula (IIIb).

5. An ion of formula (I).

20

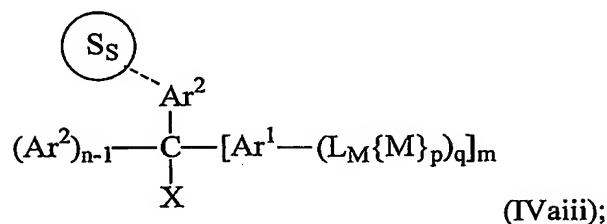
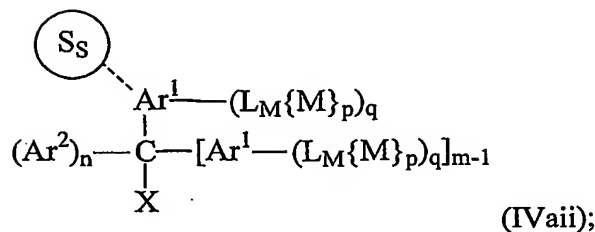
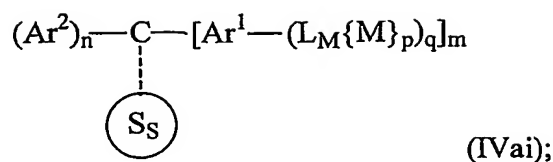
6. A compound of the formula (IIa).

7. A compound of the formula (IIb).

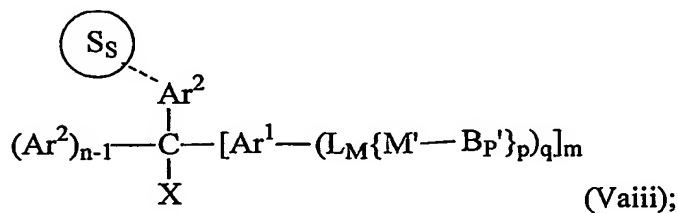
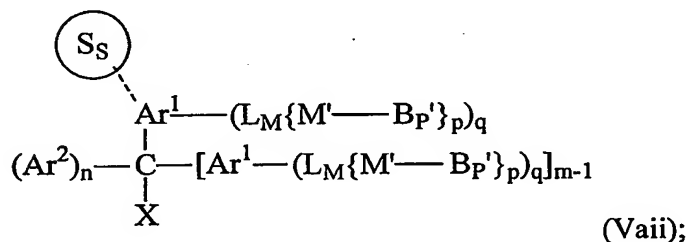
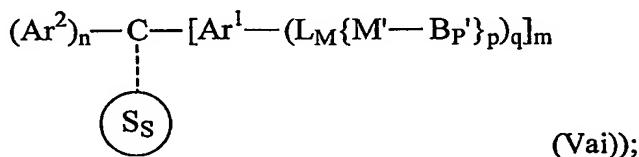
8. A method of forming an ion of formula (I) comprising the steps of:

25

(i) reacting a solid support of formula (IVai), (IVaii), or (IVaiii):



with a biopolymer, B_P, having at least one group capable of reacting with M to form a covalent linkage, to provide a modified solid support of the formula (Vai), (Vaii), or (Vaiii), respectively:



and either:

- 10 (ia) for modified solid supports of formula (Vai) cleaving the C-S_S bond between the α-carbon atom of the modified solid support of formula (Vai) and the solid support S_S to form the ion of formula (I);

(iib) for modified solid supports of formula (Vaii), either simultaneously or sequentially, cleaving the C-X bond between X and the α -carbon atom and cleaving the SS- -Ar1 bond between the solid support and the Ar1 group to form the ion of formula (I); or

(iic) for modified solid supports of formula (Vaiii), either simultaneously or sequentially, cleaving the C-X bond between X and the α -carbon atom and cleaving the SS- -Ar2 bond between the solid support and the Ar2 group to form the ion of formula (I);

where:

X, Ar¹, Ar², B_P', L_M, M, M', n, m, p and q are as defined in claim 1;

S_S is a solid support;

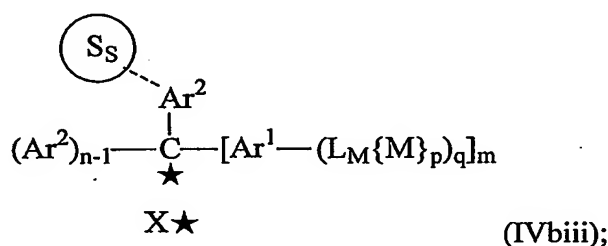
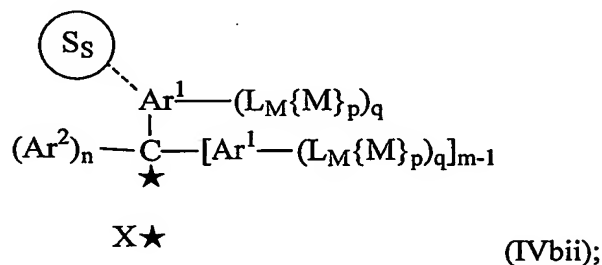
10 C---S_S comprises a cleavable bond between C and S_S;

S_S---Ar¹ comprises a cleavable bond between Ar¹ and S_S; and

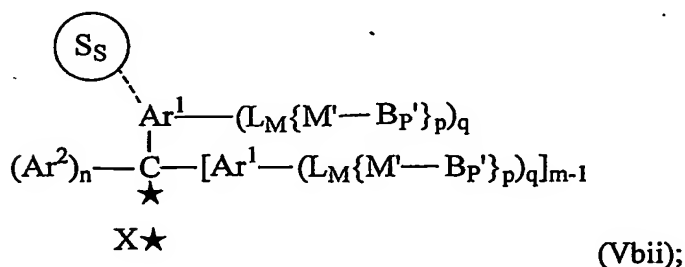
S_S---Ar² comprises a cleavable bond between Ar² and S_S.

9. A method of forming an ion of formula (I) comprising the steps of:

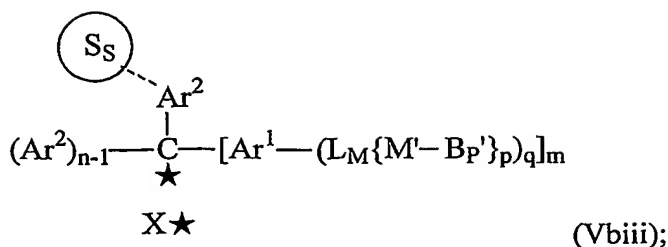
15 (i) reacting a solid support of formula (IVbii) or (IVbiii):



with a biopolymer, B_P, having at least one group capable of reacting with M to form a covalent linkage, to provide a modified solid support of the formula (Vbii) or (Vbiii), respectively:



20



and either:

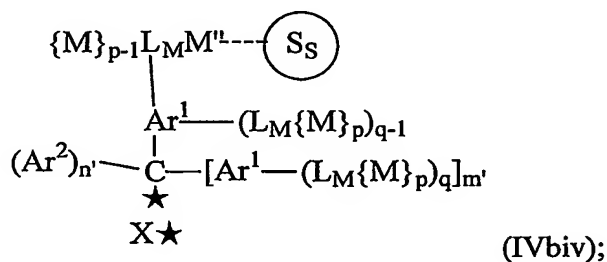
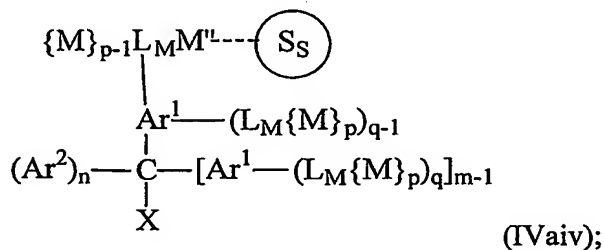
(iia) for modified solid supports of formula (Vbii), either simultaneously or sequentially, dissociating $\text{X}\star$ from the derivative of formula (Vbii) and cleaving the $\text{S}_\text{S} - \text{Ar}^1$ bond between the solid support and the Ar^1 group to form an ion of formula (I); or

(iib) for modified solid supports of formula (Vbiii), either simultaneously or sequentially, dissociating $\text{X}\star$ from the derivative of formula (Vbiii) and cleaving the $\text{S}_\text{S} - \text{Ar}^2$ bond between the solid support and the Ar^2 group to form an ion of formula (I);

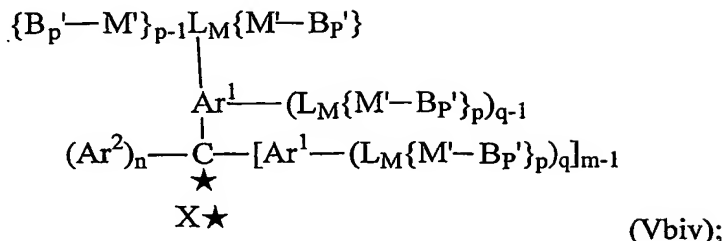
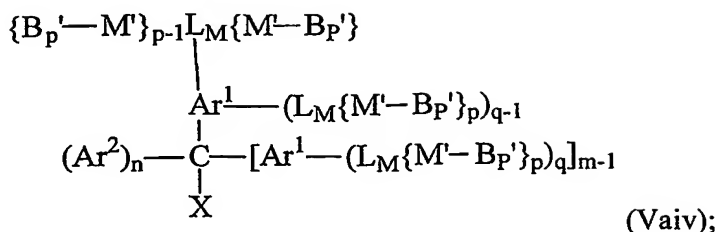
where: $\text{X}\star$, Ar^1 , Ar^2 , B_P' , L_M , M , M' , n , m , p , q , S_S , $\text{C} - \text{S}_\text{S}$, $\text{S}_\text{S} - \text{Ar}^1$ and $\text{S}_\text{S} - \text{Ar}^2$ are as defined in claim 8.

10. A method of forming an ion of formula (I) comprising the steps of:

(i) reacting a solid support of formula (IVaiv) or (IVbiv):



with a biopolymer, B_P , having at least one group capable of reacting with M to form a covalent linkage, to provide a modified solid support of the formula (Vaiv) or (Vbiv), respectively:



and either:

(iia) for modified solid supports of formula (Vaiv), cleaving the C-X bond
5 between X and the α -carbon atom to form the ion of formula (I); or

(iib) for modified solid supports of formula (Vbiv), dissociating $X\star$ from the
derivative of formula (Vbiv) to form the ion of formula (I);

where:

X, $X\star$, Ar^1 , Ar^2 , $B_{P'}'$, L_M , M, M' , p, q, n, m, and S_S are as defined in claims 8 and 9;

10 $M''-S_S$ comprises a bond between M'' and S_S ; and

M'' is the same as M except that S_S is bound to a portion of M which does not form part of
M'.

11. A solid support of the formula (IVai), (IVaii), (IVaiii), (IVaiv), (IVbii), (IVbiii) or (IVbiv).

15

12. A modified solid support of the formula (Vai), (Vaii), (Vaiii), (Vaiv), (Vbii), (Vbiii) or
(Vbiv).

13. A method of any of claims 8-10 or a product of claim 11 or 12 wherein the biopolymer is a
20 synthetic biopolymer.

14. A method or product of claim 13 wherein the synthetic biopolymer is an oligonucleotide, a
peptide or a carbohydrate.

15. A method for analysing a biopolymer, B_P, comprising the steps of:

(i) reacting the biopolymer B_P with a compound of formula (IIa) or (IIb) or a solid support of formula (IVai), (IVaii), (IVaiii), (IVaiv), (IVbii), (IVbiii) or (IVbiv);

(ii) providing an ion of formula (I); and

5 (iii) analysing the ion of formula (I) by mass spectrometry.

16. In a method for analysing a biopolymer, B_P, the improvement consisting of: (i) reacting a biopolymer, B_P with a compound of formula (IIa) or (IIb) or a solid support of formula (IVai), (IVaii), (IVaiii), (IVaiv), (IVbii), (IVbiii) or (IVbiv); (ii) providing an ion of formula (I); and (iii)

10 analysing the ion by mass spectrometry.

17. A method of claim 15 or claim 16 wherein the analysis by mass spectrometry is carried out in a spectrometer which is suitable for MALDI-TOF spectrometry.

15 18. A method of any of claims 1, 2, 8-10 or 13-17 or a product of any of claims 3-7, 11 or 12, wherein C⁺ bears a single positive charge, such that the ions of formulae (I), (IIb) and (IIIb) have the structures:

Formula (I)	$(Ar^2)_n - \overset{\oplus}{C} - [Ar^1 - (L_M - \{M' - B_P'\}_p)_q]_m$
Formula (IIb)	$(Ar^2)_n - \overset{\oplus}{C} - [Ar^1 - (L_M - \{M\}_p)_q]_m$ X^-
Formula (IIIb)	$(Ar^2)_n - \overset{\oplus}{C} - [Ar^1 - (L_M - \{M' - B_P'\}_p)_q]_m$ X^-

19. A method of any of claims 1, 2, 8-10 or 13-18 or a product of any of claims 3-7, 11, 12 or 18
20 wherein n = 2 and m = 1.

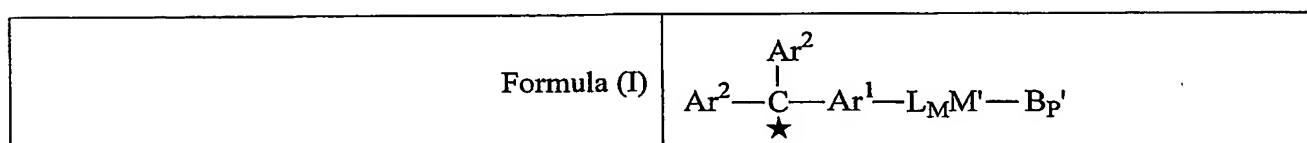
20. A method of any of claims 1, 2, 8-10 or 13-19 or a product of any of claims 3-7, 11, 12, 18 or 19 wherein p = 1, 2 or 3.

25 21. A method of any of claims 1, 2, 8-10 or 13-20 or a product of any of claims 3-7, 11, 12 or 18-20 wherein p = 1.

22. A method of any of claims 1, 2, 8-10 or 13-21 or a product of any of claims 3-7, 11, 12 or 18-21 wherein $q = 1, 2$ or 3 .

5 23. A method of any of claims 1, 2, 8-10 or 13-22 or a product of any of claims 3-7, 11, 12 or 18-22 wherein $q = 1$.

24. A method of any of claims 1, 2, 8-10 or 13-23 or a product of any of claims 3-7, 11, 12 or 18-23 wherein $n = 2$, $m = 1$, $p = 1$ and $q = 1$, such that the ion of formula (I) has the structure:



10

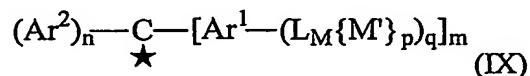
25. A method of any of claims 1, 2, 8-10 or 13-24 or a product of any of claims 3-7, 11, 12 or 18-24 wherein the biopolymer is a polymer found in biological samples.

15 26. A method or product of claim 25 wherein the biopolymer is a polypeptide, polysaccharide, or polynucleotide.

27. A method or product of claim 26 wherein the biopolymer is a polypeptide.

20 28. A method or product of any of claims 25-27 wherein the biopolymer does not readily form a molecular ion on illumination of laser light at 340 nm.

29. A method of any of claims 1, 2, 8-10 or 13-28 or a product of any of claims 3-7, 11, 12 or 18-28 wherein the ratio $m(\text{B}_P') / m(\text{IX})$ is more than 2, where $m(\text{IX})$ is the mass of the fragment (IX)



25 of the cation of formula (I) and $m(\text{B}_P')$ is the mass of the biopolymer residue B_P' .

30. A method of any of claims 1, 2, 8-10 or 13-29 or a product of any of claims 3-7, 11, 12 or 18-29 wherein M is: $-\text{NR}_2$; $-\text{SR}$; $-\text{OR}$; $-\text{B}(\text{R})\text{Y}$; $-\text{BY}_2$; $-\text{C}(\text{R})_2\text{Y}$; $-\text{C}(\text{R})\text{Y}_2$; $-\text{CY}_3$; $-\text{C}(=\text{Z})\text{Y}$;

-Z-C(=Z)Y; -C(=Z)R; -C(R)(OH)OR; -C(R)(OR)₂; -S(=O)Y; -Z-S(=O)Y; -S(=O)₂Y; -Z-S(=O)₂Y; -S(=O)₃Y; -Z-S(=O)₃Y; -P(=Z)(ZR)Y; -P(=Z)Y₂; -Z-P(=Z)(ZR)Y; -Z-P(=Z)Y₂; -P(=Z)(R)Y; -Z-P(=Z)(R)Y; or -N=C(=Z), where Y is independently a leaving group, Z is independently O, S or N(R) and R is independently H, C₁₋₈hydrocarbyl or C₁₋₈hydrocarbyl substituted with one or more A.

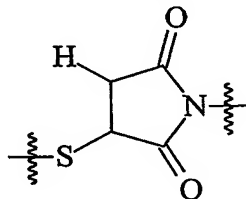
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31. A method of any of claims 1, 2, 8-10 or 13-29 or a product of any of claims 3-7, 11, 12 or 18-29 wherein M is: -N(R)-; -S-; -O-; -B(Y)-; -C(R)(Y)-; -CY₂-; -C(=O)-; -C(OH)(OR)-; or -C(OR)₂-, where Y is independently a leaving group and R is independently H, C₁₋₈hydrocarbyl or C₁₋₈hydrocarbyl substituted with one or more A.

10

32. A method of any of claims 1, 2, 8-10 or 13-29 or a product of any of claims 3-7, 11, 12 or 18-29 wherein M is: $\text{---}\overset{\text{Y}}{\underset{|}{\text{C}}}\text{---}$, where Y is a leaving group.

33. A method of any of claims 1, 2, 8-10 or 13-29 or a product of any of claims 3-7, 11, 12 or 18-29 wherein the covalent linkage is selected from those produced through the reaction of one the



following groups: -CO-NH-; biotin-(strept)avidin; ; or -NH-CS-NH-.

34. A method of any of claims 1, 2, 8-10 or 13-33 or a product of any of claims 3-7, 11, 12 or 18-33 wherein L_M is O or S.

20

35. A method of any of claims 1, 2, 8-10 or 13-33 or a product of any of claims 3-7, 11, 12 or 18-33 wherein L_M is -E^M-, -(D^M)_t-, -(E^M-D^M)_t-, -(D^M-E^M)_t-, -E^M-(D^M-E^M)_t- or -D^M-(E^M-D^M)_t- (in the orientation Ar¹-(L_M{M}_p)_q or Ar¹-(L_M{M'}_p)_q, as appropriate),

where:

25 a sufficient number of linking covalent bonds, in addition to the covalent bonds at the chain termini shown, are provided on groups E^M and D^M for linking the p instances of M (or M') groups;

D^M is independently C₁₋₈hydrocarbylene or C₁₋₈hydrocarbylene substituted with one or more A;

E^M (in the orientation Ar¹-(L_M{M}_p)_q or Ar¹-(L_M{M'}_p)_q, as appropriate) is independently -Z^M-, -C(=Z^M)-, -Z^MC(=Z^M)-, -C(=Z^M)Z^M-, -Z^MC(=Z^M)Z^M-, -S(=O)-, -Z^MS(=O)-, -S(=O)Z^M-,

$-Z^M S(=O)Z^M-$, $-S(=O)_2-$, $-Z^M S(=O)_2-$, $-S(=O)_2 Z^M-$, $-Z^M S(=O)_2 Z^M-$, where Z^M is independently O, S or N(R^M) and where R^M is independently H, C_{1-8} hydrocarbyl (e.g. C_{1-8} alkyl) or C_{1-8} hydrocarbyl substituted with one or more A; and

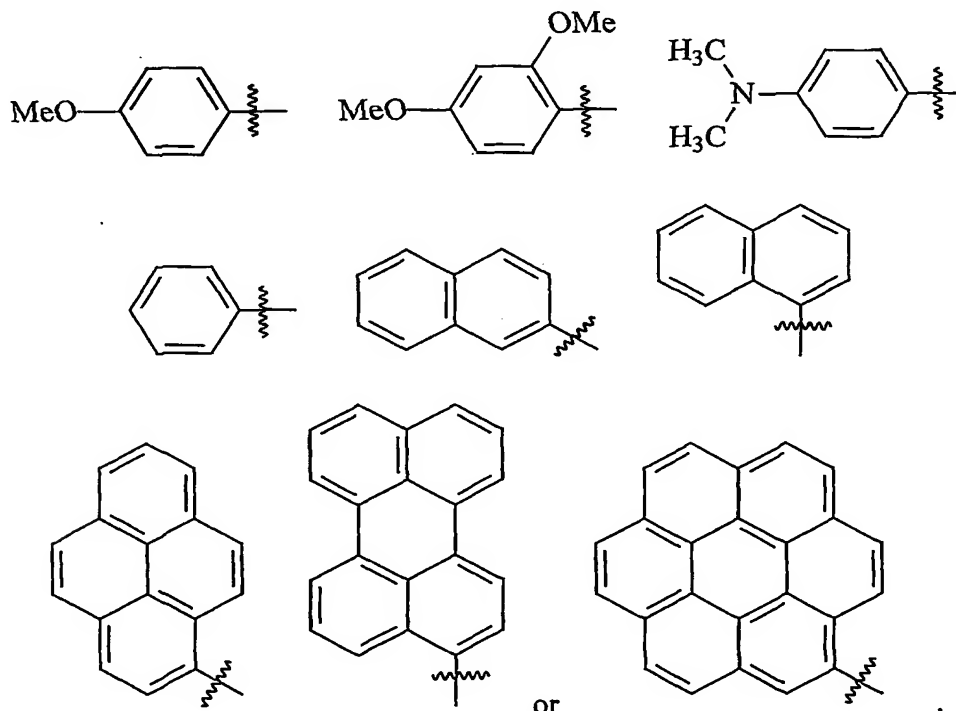
$t = 1$ or more.

5

36. A method of any of claims 1, 8, 10 or 13-35 or a product of any of claims 3, 6, 11, 12 or 18-35 wherein the group X is halogen, hydroxy, C₁₋₈hydrocarbyloxy, C₁₋₈hydrocarbyloxy substituted with one or more A, C₁₋₈heterohydrocarbyloxy, C₁₋₈heterohydrocarbyloxy substituted with one or more A, mesyl, tosyl, pentafluorophenyl, -O-succinimidyl -S-succinimidyl, or phenoxy substituted with one or more A.

37. A method of any of claims 1, 2, 8-10 or 13-36 or a product of any of claims 3-7, 11, 12 or 18-36 wherein Ar² is independently cyclopropyl, cyclopropyl substituted with one or more A, aryl, aryl substituted with one or more A, heteroaryl, or heteroaryl substituted with one or more A.

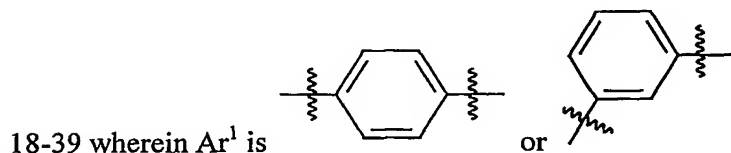
38. A method of any of claims 1, 2, 8-10 or 13-37 or a product of any of claims 3-7, 11, 12 or 18-37 wherein Ar² is



39. A method of any of claims 1, 2, 8-10 or 13-38 or a product of any of claims 3-7, 11, 12 or 18-38 wherein Ar^1 is independently cyclopropylene, cyclopropylene substituted with one or more A, arylene, arylene substituted with one or more A, heteroarylene, or heteroarylene substituted with one or more A.

5

40. A method of any of claims 1, 2, 8-10 or 13-39 or a product of any of claims 3-7, 11, 12 or



41. A method of any of claims 1, 2, 8-10 or 13-40 or a product of any of claims 3-7, 11, 12 or 18-40 wherein L^5 is O or S.

42. A method of any of claims 1, 2, 8-10 or 13-40 or a product of any of claims 3-7, 11, 12 or 18-40 wherein L^5 is $-E^5-$, $-(D^5)_{t'}$, $-(E^5-D^5)_{t'}$, $-(D^5-E^5)_{t'}$, $-E^5-(D^5-E^5)_{t'}$ or $-D^5-(E^5-D^5)_{t'}$,

where:

15 D^5 is independently C_{1-8} hydrocarbylene or C_{1-8} hydrocarbylene substituted with one or more A;

E^5 is independently $-Z^5-$, $-C(=Z^5)-$, $-Z^5C(=Z^5)-$, $-C(=Z^5)Z^5-$, $-Z^5C(=Z^5)Z^5-$, $-S(=O)-$, $-Z^5S(=O)-$, $-S(=O)Z^5-$, $-Z^5S(=O)Z^5-$, $-S(=O)_2-$, $-Z^5S(=O)_2-$, $-S(=O)_2Z^5-$, $-Z^5S(=O)_2Z^5-$, where Z^5 is independently O, S or $N(R^5)$ and where R^5 is independently H, C_{1-8} hydrocarbyl or C_{1-8} hydrocarbyl substituted with one or more A; and

$t' = 1$ or more.